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Review

Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater – A review on concentrations and distribution coefficients

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h i g h l i g h t s

- log_{K_{oc}} coefficients for PFOS and PFOA are similar for soils and sewage sludge.
- Field-based distribution coefficients are larger than lab-based coefficients.
- Dissipation times from soils may be underestimated using lab-based coefficients.
- Groundwater and surface waters are the main sinks for PFOA and PFOS.

a r t i c l e i n f o

Article history:

Received 8 August 2012

Received in revised form 8 February 2013

Accepted 9 February 2013

Available online 14 March 2013

Keywords:

Groundwater contamination

Persistent organic pollutants

Bioaccumulation

Food chain

a b s t r a c t

The sorption of perfluorinated compounds (PFCs) to soils and sediments determines their fate and distribution in the environment, but there is little consensus regarding distribution coefficients that should be used for assessing the environmental fate of these compounds. Here we reviewed sorption coefficients for PFCs derived from laboratory experiments and compared these values with the gross distribution between the concentrations of PFCs in surface waters and sediments or between wastewater and sewage sludge. Sorption experiments with perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) suggest that their sorption can be described reasonably well as a partitioning-like process with an average log_{K_{oc}} of approximately 2.8 for PFOA and 3.0 for PFOS. However, median concentrations in sediments (PFOA, 0.27 ng g⁻¹; PFOS, 0.54 ng g⁻¹) or sewage sludge (PFOA, 37 ng g⁻¹; PFOS, 69 ng g⁻¹) in relation to median concentrations in surface water (PFOA, 3 ng l⁻¹; PFOS, 3 ng l⁻¹) or wastewater treatment effluent (PFOA, 24 ng l⁻¹; PFOS, 11 ng l⁻¹), suggest that effective log_{K_{oc}} distribution coefficients for the field situation may be close to 3.7 for PFOA and 4.2 for PFOS. Applying lab-based log_{K_{oc}} distribution coefficients can therefore result in a serious overestimation of PFC concentrations in water and in turn to an underestimation of the residence time of PFOA and PFOS in contaminated soils. Irrespective of the dissipation kinetics, the majority of PFOA and PFOS from contaminated soils will be transported to groundwater and surface water bodies.

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1. Introduction

Perfluorinated compounds (PFCs) are produced since the 1950s and have found wide application e.g., in the metal industry, as protective coatings for paper and textile fabrics, in the electronics industry for the production of semi-conductors or as a component of fire-fighting foam (Tsai et al., 2002; Brooke et al., 2004; Lindstrom et al., 2011). This wide-spread use has resulted in a release of PFCs into the environment either from direct sources such as the manufacturing of PFCs and the use of products containing PFCs, as well as from indirect sources like reaction impurities or degradation of precursors (Boulangier et al., 2005; Prevedouros et al., 2006; Lau et al., 2009; Lindstrom et al., 2011). It has been estimated that nearly 80% of perfluorinated carboxylic acids that have been released into the environment can be related to direct contamination that occurred during fluoropolymer manufacture and use (Prevedouros et al., 2006; Wang et al., 2009). At present, PFCs are ubiquitously found in diverse environmental compartments at concentrations ranging from pg kg^{-1} levels to lg kg^{-1} levels all around the world, thus posing a global risk from human uptake – which depends on the type of compounds and the length of the fluorinated carbon chain (Houde et al., 2006; Conder et al., 2008; Rayne and Forest, 2009a; Fromme et al., 2009; van Asselt et al., 2011; Domingo, 2012). The global distribution of these compounds after more than 50 years of manufacture and use is caused by the extreme resistance of PFCs to thermal or biological breakdown and their high water-solubility (Key et al., 1997; Fricke and Lahl, 2005; Burns et al., 2008; Goss, 2008; Rayne and Forest, 2009a; Liou et al., 2010).

In the context of risk analysis, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) have attracted most attention because these compounds commonly constitute a high proportion of environmental contaminations involving PFCs (Brooke et al., 2004; Dimitrov et al., 2004; Lehmler, 2005; Lindstrom et al., 2011). A recent survey of European groundwater for example showed that PFOS accounted for 66% and PFOA for 48% of detected PFC compounds (Loos et al., 2010). The transfer of PFCs from contaminated sites into water bodies or plants, as well as from wastewater treatment plants into receiving surface waters is determined by the compounds sorption to soil or sewage sludge. Yet it remained unclear, which sorption or distribution coefficients should be used for assessing the fate of PFCs and related risks in different environmental compartments. We therefore reviewed the existing knowledge regarding sorption of PFOA and PFOS to soils, sediments, and sewage sludge. One goal of the review was to assess the variability of sorption coefficients for different sorbents. In order to test how good published sorption coefficients reflect the actual distribution of PFOA and PFOS between surface waters and sediments or between sewage and sewage sludge, we also reviewed the concentrations of these compounds in water, sediment, sewage and sewage sludge and calculated “global” distribution coefficients that can be compared to experimentally determined coefficients. Finally, we summarized published PFOA and PFOS concentrations in soils and assessed the sensitivity of dissipation from soil and plant uptake dynamics towards the observed variability of sorption or distribution coefficients. Rayne and Forest (2009a) provided an excellent review of physicochemical properties, concentration levels, and patterns of perfluorinated sulfonic and carboxylic acids in waters and wastewaters. We think that our brief review presented here is justified because a significant number of new sorption studies have been published since then and because the review of Rayne and Forest (2009a) did not cover soils, sediments and sewage sludge, thus preventing a meta-analysis of the overall distribution between aqueous phase and solids in natural environments. One factor that provided a challenge in our analysis was the treatment of values below the detection limit or quantification limit published in the literature.

Omitting these values would have created a bias towards high concentrations. Therefore we decided to assign such very low PFC concentrations either with a value of the full respective detection limit or quantification limit, of its half, or with a value of zero, and included the resulting uncertainty in the analyses.

1.1. Sorption of PFOA and PFOS to soils, sediments, and sewage sludge

Several studies on the sorption behavior of PFCs in soils are available in scientific literature (Higgins and Luthy, 2006; Johnson et al., 2007; Chen et al., 2009; Ahrens et al., 2011). The studies showed that sorption of PFCs is frequently non-linear and best described by Freundlich (Higgins and Luthy, 2006) or Langmuir isotherms (Johnson et al., 2007). Nevertheless linear isotherms have also been successfully used (Ahrens et al., 2011). Freundlich coefficients ranged from 0.75 to 1.00 with an average of 0.90 in the study of Higgins and Luthy (2006). A comparison of all PFC sorption data for soils and sediments of varying organic matter and iron oxide content indicated that organic matter content is its dominating controlling factor (Higgins and Luthy, 2006). In the sorption studies of Li et al. (2012), sorption of PFOA to sediments was mainly governed by black carbon content, iron oxide content, clay content, and specific surface area, hence suggesting that PFOA sorption is predominantly an entropy-driven process. The fact that cationic and anionic surfactants can drastically change the sorption of PFOS to natural sediments (Pan et al., 2009) also supports the idea of entropy-driven sorption. Together with the Freundlich exponent close to unity reported by Higgins and Luthy (2006), this indicates that PFCs sorption to soils and sediments can be described reasonably well as a partitioning process, with the K_{oc} distribution coefficient increasing by 0.5–0.8 log units per CF_2 group (e.g., Ahrens et al., 2010; Labadie and Chevreuil, 2011). In spite this nearly partitioning-like behavior of PFCs sorption, strong effects of solution Ca^{2+} concentration and pH on sorption have been reported. In a recent study a decrease in PFOS and PFOA sorption to alumina surfaces has been shown with an increase in ionic strength due to a compression of the electrical double layer (Wang and Shih, 2011). These effects can be explained by variations of the electrostatic Coulomb potential of a sorbent as a function of pH and cation concentration (Higgins and Luthy, 2006; Chen et al., 2009; You et al., 2010). Sorption of PFOA to goethite exceeded sorption to river sediments and illite in experiments of Li et al. (2012), which could also be explained by electrostatic interactions between negatively charged PFOA and positively charged Fe-oxide surfaces and by the large surface area of the oxides. Higgins and Luthy (2007) thus proposed a general sorption model describing the effect of electrostatic interactions on sorption of PFOA, PFOS, and other anionic surfactants (Eq. (1)),

$$K_d = k_{oc} f_{oc} \frac{F_{access} V_w}{Q_{oc} V_i} \exp \left(\frac{\gamma_1 DG_{hyd,i}}{RT} \right) \exp \left(\frac{z_i F w}{RT} \right) \quad (1)$$

with f_{oc} as dimensionless fraction of organic carbon in soil or sediment, F_{access} as dimensionless volumetric fraction of organic carbon accessible for the sorbate (fitting parameter), V_w as molar volume of water (0.018 l mol^{-1}), V_i as molar volume of the sorbate (l mol^{-1}), Q_{oc} as density of organic matter ($\sim 0.5 \text{ kg l}^{-1}$), $\gamma_1 DG_{hyd,i}$ as Gibbs free energy of hydrophobic interactions estimated from excess free energies of aqueous solutions (PFOA, 25.5 kJ mol^{-1} ; PFOS, 30.0 kJ mol^{-1}), z_i as valence of the sorbate (~ 1 for PFOA and PFOS), F as Faraday constant ($9.6 \times 10^6 \text{ C mol}^{-1}$), w as electrostatic surface potential of organic matter (V) depending among other factors mainly on pH, R as ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T denoting the temperature in Kelvin.

However, variations in Coulomb potential of organic matter were unable to explain the observed non-linearity of experimental

Table 1
Published distribution coefficients derived from laboratory sorption experiments ($\log K_d$, $\log K_{oc}$).

Sample	$\log K_d$ ($\log l\ kg^{-1}$)	$\log K_{oc}$	References
PFOS			
Five sediments with C_{org} of 0.56–9.66% dithionite–citrate–bicarbonate extractable iron of 116–1025 l mol/g	–	2.7	Higgins and Luthy (2006)
Ottawa sand standard	2.81	–	Johnson et al. (2007)
Kaolinite	5.31	2.4	Johnson et al. (2007)
Goethite	7.88	–	Johnson et al. (2007)
High iron sand standard	8.90	–	Johnson et al. (2007)
Lake Michigan sediment	7.52	2.4–2.6	Johnson et al. (2007)
Clay	18.3	2.8	3 M corp. cited in Johnson et al. (2007)
Clay loam	9.72	2.6	3 M corp. cited in Johnson et al. (2007)
Sandy loam	35.3	3.1	3 M corp. cited in Johnson et al. (2007)
River sediment	7.42	2.8	3 M corp. cited in Johnson et al. (2007)
Water treatment sludge	120	2.5	3 M corp. cited in Johnson et al. (2007)
Paddy soil (0.91% C_{org}) at $c(\text{water}) = 5.0\ l\ g^{-1}$	–	3.3	Chen et al. (2009)
Crude oil spiked to soil	–	4.2–4.4	Chen et al. (2009)
Oil-derived black carbon (diesel soot), $c(\text{water}) = 5–50\ l\ g^{-1}$ at pH = 5.05	–	3.0–3.1	Chen et al. (2009)
Aquifer sediment Washington County, USA ($t = 0$)	0.1	2.5	Ferrey et al. (2009)
Aquifer sediment Washington County ($t = 574\ d$)	± 0.7	2.8	Ferrey et al. (2009)
Taihu Lake	–	2.9 ± 0.6	Yang et al. (2011)
Sediment 1	1.2	4.7	Ahrens et al. (2011)
Sediment 2	1.2	3.0	Ahrens et al. (2011)
Sediment 3	1.9	3.8	Ahrens et al. (2011)
Average PFOS ($\log l\ kg^{-1}$)		3.0	
Standard deviation PFOS ($\log l\ kg^{-1}$)		0.7	
Coefficient of variation PFOS (%)		21	
Median PFOS ($\log l\ kg^{-1}$)		2.8	
PFOA			
Five sediments with C_{org} of 0.56–9.66% dithionite–citrate–bicarbonate extractable iron of 116–1025 l mol/g	–	2.1	Higgins and Luthy (2006)
Aquifer sediment Washington County, Minn., USA ($t = 0$)	–0.01	3.5	Ferrey et al. (2009)
Aquifer sediment Washington County ($t = 574\ d$)	–1.16	2.3	Ferrey et al. (2009)
Sediment 1	0.96	4.5	Ahrens et al. (2011)
Sediment 2	0.67	2.5	Ahrens et al. (2011)
Liao river sediment	–	2.3 ± 0.4	Yang et al. (2011)
Taihu Lake sediment	–	2.3 ± 0.6	Yang et al. (2011)
Yangtse sediment CQ	–0.77	1.5	Li et al. (2012)
Yangtse sediment ZG	–0.62	1.4	Li et al. (2012)
Yangtse sediment WH	–0.72	1.3	Li et al. (2012)
Yangtse sediment NJ	–0.89	1.3	Li et al. (2012)
Yangtse sediment CMW	–0.82	1.3	Li et al. (2012)
Yangtse sediment CME	–0.92	1.6	Li et al. (2012)
Average PFOA ($\log l\ kg^{-1}$)	–	2.1(2.8)	
Standard deviation PFOA ($\log l\ kg^{-1}$)	–	1.0(0.9)	
Coefficient of variation PFOA (%)	–	45(32)	
Median PFOA ($\log l\ kg^{-1}$)	–	2.1(2.3)	

Values in brackets excluding values of Li et al. (2012).

sorption isotherms of Higgins and Luthy (2007). Nevertheless, Higgins and Luthy (2007) argued that specific interactions of the carboxylic and sulfonate functional groups of PFCs were unlikely to affect their sorption, because sulfonated fluorocarbons sorbed stronger than carboxylated ones, despite the former are less prone to form complexes with metal cations. This view is supported by sorption experiments with minerals, which showed that the surface area normalized sorption of PFOS decreased in the order Ottawa sand standard > high iron sand > kaolinite > goethite (Johnson et al., 2007), i.e., with increasing surface reactivity. The different sorption of sulfonated and carboxylated PFCs was also explained by the different volume of the functional groups and adsorbent size giving rise to different DG of the underlying hydrophobic interactions (Higgins and Luthy, 2007; Ochoa-Herrera and Sierra-Alvarez, 2008; Qu et al., 2009; Yu et al., 2009a).

In summary, it appears that an entropy-driven exclusion of PFOA and PFOS from the aqueous phase towards organic, as well as mineral, surfaces governs sorption of these compounds, which is further modulated by the Coulomb potential of the surfaces and the thickness of the electric double layer. Deviations of the general sorption model of Higgins and Luthy (2007) from experimental data

can possibly be explained by the neglected contribution of mineral surfaces to sorption. Most likely, the correlation between organic carbon content, clay content, oxide content and specific surface area across different soils and sediments is one reason why normalizing sorption coefficients to the organic carbon content of soils and sediments reduces their scatter so efficiently.

Experimental $\log K_{oc}$ values for PFOS for different soils and sediments available in public literature are therefore remarkably similar, showing a coefficient of variation of only 21% with an average of 3.0 (Table 1). For PFOA, the published $\log K_{oc}$ values exhibit a coefficient of variation of 32% with an average of $\log K_{oc}$ of 2.8 (Table 1). The difference of 0.2 log units between the average $\log K_{oc}$ of PFOA and PFOS is smaller than the difference of 0.5–0.6 log units that could be expected based on the difference in chain length (see above). Data of Li et al. (2012) are indeed approximately one order of magnitude smaller than other published values, thus increasing the difference between the average $\log K_{oc}$ of PFOA and PFOS (Tables 1 and 2). Unlike the other published sorption studies the experiments of Li et al. (2012) were conducted with radiolabeled PFOA, but it is unclear whether this different experimental approach is responsible for the observed difference in sorption

Table 2
Concentrations of PFOA and PFOS in soils.

Sample origin	PFOA (ng g ⁻¹)	PFOS (ng g ⁻¹)	References
Shanghai agricultural land SO 1	20.4(5 ^a)	10.4(7 ^a)	Li et al. (2010)
Shanghai agricultural land SO 3	3.3(7 ^a)	9.2(9 ^a)	Li et al. (2010)
Shanghai agricultural land SO 6	44.0(4 ^a)	9.6(2 ^a)	Li et al. (2010)
Shanghai agricultural land SO 7	35.2(4 ^a)	9.3(8 ^a)	Li et al. (2010)
Shanghai residential & industrial area SO 2	42.8(6 ^a)	9.5(5 ^a)	Li et al. (2010)
Shanghai residential & industrial area SO 4	47.5(7 ^a)	10.3(6 ^a)	Li et al. (2010)
Shanghai residential & industrial area SO 5	46.5(5 ^a)	9.5(7 ^a)	Li et al. (2010)
Shanghai residential & industrial area SO 8	42.3(7 ^a)	8.6(2 ^a)	Li et al. (2010)
Chicago Water Reclamation district with short term (3 year) application of biosolids	–	2–11	Sepulvado et al. (2011)
Chicago Water Reclamation district with long-term or general multiple application of biosolids	–	5.5–483	Sepulvado et al. (2011)
Agricultural sandy loam (P-1)	0.1(0.02 ^b)	–	Washington et al. (2008)
Sandy clay loam from picnic area (Picnic)	0.6(0.05 ^b)	–	Washington et al. (2008)
Sandy loam topsoil (Cownt)	0.7(0.05 ^b)	–	Washington et al. (2008)
Guanting reservoir area	0.9	2.8	Wang and Shih (2011)
Chinese soil (Beijing)	0.3	0.4	Yuan-Yuan et al. (2010)
NC04, North Carolina, USA	31.7	2.6	Strynar et al. (2012)
NC02, North Carolina, USA	15.6	0.6	Strynar et al. (2012)
NC05, North Carolina, USA	8.4	1.5	Strynar et al. (2012)
J28-3, Osaka, Japan	21.5	0.6	Strynar et al. (2012)
TX03, Houston, Texas, USA	2.7	2.2	Strynar et al. (2012)
KY01, Richmond, Kentucky, USA	2.1	1.6	Strynar et al. (2012)
IN01, W. Lafayette, Indiana, USA	2.1	–	Strynar et al. (2012)
M2, Mexico City, Mexico	0.8	10.1	Strynar et al. (2012)
J1-2, Hokaido, Japan	1.8	5.2	Strynar et al. (2012)
NC07, Laurel Fork, North Carolina, USA	1.3	2.5	Strynar et al. (2012)

^a Relative standard deviation, n = 3.

^b Standard deviation of measurements using Waters system and sample pretreatment with NaOH.

coefficients. Nevertheless, the similarity of published K_{oc} values for PFOS together with indications for a predominantly partitioning like sorption give rise to the hope that binding of PFOS and PFOA in soil for predicting transfer into plants or leaching to groundwater can be estimated with acceptable certainty from published sorption coefficients, or by using established structure-property relationships when considering the organic carbon content of soils, as suggested by Rayne and Forest (2009a).

It is important to note in this context that PFCs are not lipophilic, but rather “proteinophilic” (Conder et al., 2008; Rayne and Forest, 2009a,b). In line with this proteinophilic behavior of PFCs, it has been argued that PFC concentrations in Shanghai soils may not be related to soil organic carbon contents because in fact the protein content of organic matrices also contributes to PFC sorption (Li et al., 2010). In general, however, soil protein and total organic matter content are also correlated, as reflected by C/N ratios around 10–20 for a broad range of soils (Blume et al., 2009).

1.2. Concentrations and distribution of PFOA and PFOS in surface water, sediments, wastewater treatment plant effluent, and sewage sludge

To evaluate how well experimental K_{oc} distribution coefficients reflect the distribution of PFOA and PFOS between surface water and sediments as well as between wastewater treatment effluent and sewage sludge, we summarized their concentrations in these environmental compartments (see the MS-Excel file in the electronic Supplementary data). Concentrations of PFOA in surface water that have been reported in publicly available literature vary widely over more than seven orders of magnitude (Fig. 1, Hansen et al., 2002; Taniyasu et al., 2003; Saito et al., 2004; Guruge et al., 2007; So et al., 2007; Wei et al., 2007; Becker et al., 2008a; Furdui et al., 2008; Lien et al., 2008; Loos et al., 2008; Ahrens et al., 2009a,b; Jin et al., 2009; Quinete et al., 2009; Teng et al., 2009). Half of the reported concentrations fall however within a

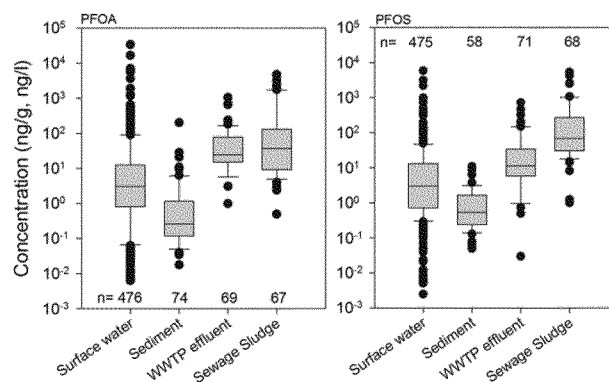


Fig. 1. Concentrations of PFOA and PFOS in surface water, surface water sediments, wastewater treatment plant effluent, and sewage sludge. WWTP, wastewater treatment plant.

rather low range between 0.8 and 13 ng l⁻¹ with a median concentration of 3.1 ng l⁻¹. When assuming that all concentrations reported to be smaller than the detection limit are zero, this median concentration reduces to 2.8 ng l⁻¹. When setting these concentrations equal to the detection limit of the respective studies, the median concentration increases to 3.3 ng l⁻¹. These three values differ less than 17% from their arithmetic mean, nevertheless it will be important to assess how the treatment of values smaller than detection limit affects calculated distribution coefficients.

The distribution in Fig. 1 shows that PFOA concentrations exceeding approximately 100 ng l⁻¹ are likely to be indicative of pollution point sources connected to the surface water body. Concentrations reported for surface waters in Germany and The Netherlands are among the top three of a concentration ranking list, with highest maximum concentrations found among all studies

(Fig. 2, Skutlarek et al., 2006; McLachlan et al., 2007; Becker et al., 2008a; Ahrens et al., 2009a,b; Möller et al., 2010). Concentrations for Germany and The Netherlands are presented in combination, because surface waters in the Rhine watershed in both countries were influenced by a heavy contamination in the Möhne and Ruhr catchment area (Skutlarek et al., 2006), to which the extreme values are related. This shows that regional average levels of PFOA in surface water that can be extracted from the literature are likely to have been strongly influenced by single pollution events, so that their indicative value for the general exposure of the environment to PFOA in larger regions is limited.

Concentrations of PFOS in surface water cover a similar range as PFOA concentrations with a median concentration of 3.2 ng l^{-1} (Fig. 1; Saito et al., 2003; Taniyasu et al., 2003; Nakayama et al., 2007; So et al., 2007; Becker et al., 2008a,b; Furdul et al., 2008; Ahrens et al., 2009a,b; Jin et al., 2009; Quinete et al., 2009; Teng et al., 2009). This value is not changed by setting all concentrations smaller than detection limit to zero, whereas it increases to 3.3 ng l^{-1} by using the respective detection limits instead of their half for the calculation of representative average. Overall, concentrations of PFOS and PFOA in surface waters are significantly correlated (Kendalls tau rank correlation coefficient of 0.52, $r^2 = 0.53$; Fig. 3). Concentrations in German and Dutch surface waters are not among the top three of our concentration ranking list (Skutlarek et al., 2006; Ahrens et al., 2009a,b; Möller et al., 2010), probably reflecting the stronger retention of PFOS in comparison to PFOA in the contaminated soils of the Ruhr and Möhne catchment area. Similarly to the results for PFOA concentrations, this finding indicates that the distribution of PFOS observations in individual countries is influenced to a large degree by individual pollution cases, which precludes their interpretation as an indicator of regio-

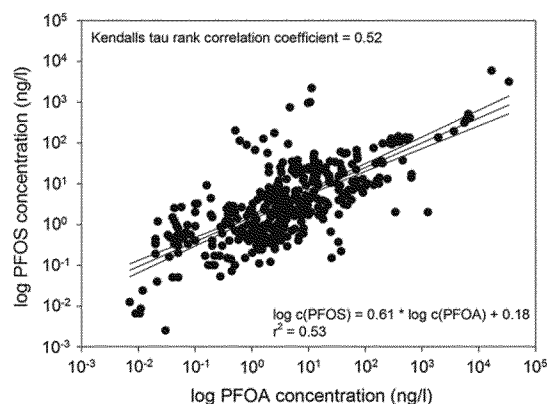


Fig. 3. Correlation between PFOS- and PFOA-concentrations of surface water samples.

nal background levels of this compound (Moody et al., 2002; Kärrman et al., 2011).

Less data on PFOA concentrations in sediments have been reported in the public literature (Fig. 1, Higgins et al., 2005; Senthil Kumar et al., 2007; Becker et al., 2008b; Ahrens et al., 2009a,b; Bao et al., 2009; Clara et al., 2009; Ma and Shih, 2010; Zushi et al., 2010). The median concentration in sediment that can be extracted from the (limited) literature is 0.3 ng g^{-1} (arithmetic mean, 5 ng g^{-1}). This median value remains unchanged, irrespective of how we treat values below the LOD, i.e., irrespective of whether we used a value of zero, half or full detection limit for the calculations. In an attempt to derive a kind of “global K_d ” value for the distribution of PFOA between water and sediment, we thus simply divided the median sediment concentration in ng kg^{-1} by the median surface water concentration of 3 ng l^{-1} resulting in a value of 85 l kg^{-1} ($\log K_d = 1.9$). Assuming an average organic carbon content of 1.7% in sediments (mean of studies from which PFOA concentrations in sediments were considered), our “back of an envelope” calculation would result in a “global” $\log K_{oc}$ of 3.7 for PFOA (with $K_{oc} = K_d/0.017$). Again, this value is not affected by using a value of zero or by using a value equal to the respective detection limit for concentrations smaller than detection limit. Similarly, dividing the median PFOS sediment concentration of 535 ng kg^{-1} by the median PFOS surface water concentration results in a “global average” K_d value of 178 ($\log K_d = 2.3$). The “global average” $\log K_{oc}$ for PFOS in sediments (assuming an average sediment C_{org} concentration of 1.7%) then equals 4.0. Using a value of zero for data smaller than the detection limit reduces this $\log K_{oc}$ to 3.8, setting data smaller than the detection limit equal to this limit increases the $\log K_{oc}$ to 4.2.

As expected, concentrations of PFOA in effluents of wastewater treatment plants (WWTPs) tended to exceed concentrations in surface water by approximately a factor of 12 (ratio of medians, Fig. 1; Boulanger et al., 2005; Sinclair and Kannan, 2006; Loganathan et al., 2007; Becker et al., 2008a; Bossi et al., 2008; Guo et al., 2008; Plumlee et al., 2008; Ahrens et al., 2009a,b; Yu et al., 2009b; Li et al., 2010). The ratio of reported PFOA concentrations in sewage sludge (and some samples of solids suspended in wastewater) in relation to effluent concentrations is much higher than the ratio of sediment concentrations in relation to surface water concentrations. This observation is probably at least partly related to the higher organic carbon contents of sewage sludge compared with the organic carbon contents of sediments. The “global average” K_d that we could calculate from the median concentrations of PFOA in WWTP effluent of 24 ng l^{-1} and sewage sludge (37 ng g^{-1}) equals 1535 l kg^{-1} ($\log K_d = 3.2$). Considering an average dry matter organic carbon content of 31% for sewage sludge

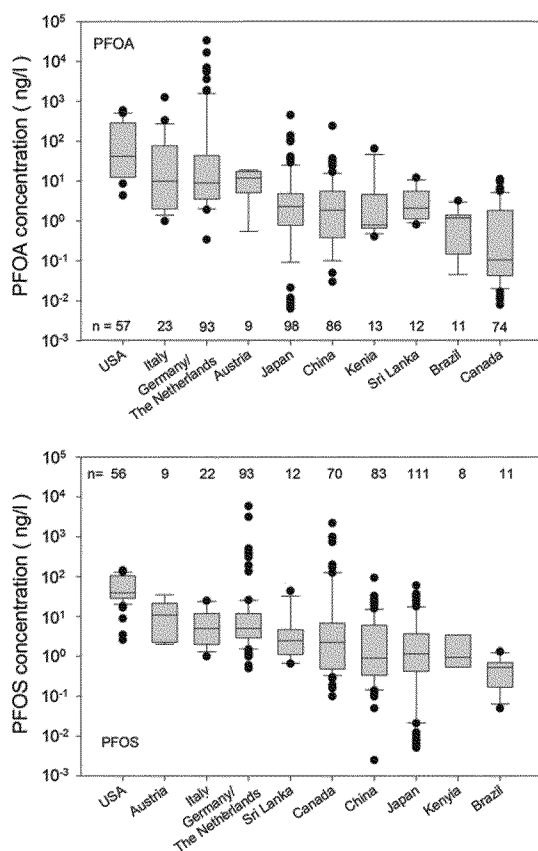


Fig. 2. Distribution of PFOA concentrations in surface waters in different countries.

gives a global average $\log K_{oc}$ of 3.7, which is surprisingly similar to that calculated for sediments (see above). Concentrations of PFOS in WWTP effluent exceed concentrations in surface water by a factor of four and median sludge concentrations are even two orders of magnitude larger than sediment concentrations (Fig. 1). “Global average” $\log K_d$ and K_{oc} values for sewage sludge are thus 3.8 and 4.3, respectively. In both cases the global $\log K_{oc}$ values for PFOA and PFOS in sewage sludge are not affected by the way we treat values below the detection limit. The difference in $\log K_{oc}$ between PFOS and PFOA for sewage sludge hence fits in with the 0.5–0.8 log units increase of the distribution coefficient per CF_2 -group (e.g., Labadie and Chevreuil, 2011).

When interpreting our “global” distribution coefficients, it is important to keep in mind that for sediment samples much less data are available than for surface waters and that our approach of calculating these distribution coefficient does not consider any spatial relationship between sampling points. Ahrens et al. (2010), Kwadjik et al. (2010) and Labadie and Chevreuil (2011) related sediment or suspended matter concentrations to surface water concentrations of the same locations in order to derive “field-based” distribution coefficients. These “field-based” $\log K_{oc}$ distribution coefficients ranged from 1.9 to 3.5 for PFOA (mean, 2.7) and from 3.2 to 4.8 (mean, 3.9) for PFOS, being smaller than our “global” $\log K_{oc}$ values for PFOA and similar to the ones for PFOS. Overall, the field-based distribution coefficients of Ahrens et al. (2010), Kwadjik et al. (2010) and Labadie and Chevreuil (2011) as well as our “global” distribution coefficients are consistently larger than distribution coefficients derived from laboratory batch experiments, which suggests that sorption of PFOA and PFOS under field conditions might be stronger than would be estimated from lab experiments, e.g. because of much smaller concentrations encountered in the field and the principally non-linear nature of sorption isotherms that is not reflected in laboratory batch experiments conducted at higher concentrations, and/or because ageing and sorption hysteresis in general enhances the binding of older contaminations in environmental samples (e.g., Luthy et al., 1997; Ciglasch et al., 2008; Förster et al., 2009).

1.3. Soil concentrations of PFOA and PFOS and sensitivity of the fate of soil contaminations towards variations in the $\log K_{oc}$ distribution coefficient

Data regarding concentrations of PFCs in soils are sparse in the scientific literature (Washington et al., 2008; Li et al., 2010; Yuan-Yuan et al., 2010; Wang and Shih, 2011; Strynar et al., 2012) and reported concentrations are often smaller than the detection limits. Based on the analysis of 10 soil samples from each of six countries (USA, China, Japan, Norway, Greece, and Mexico), Strynar et al. (2012), estimated a global median soil concentration of 0.124 ng g^{-1} for PFOA and 0.472 ng g^{-1} for PFOS. Li et al. (2010) reported much higher concentrations of PFOA and PFOS for soils from Shanghai, China. Contrary to their expectations, agricultural soils were not always less polluted than soils from residential or industrial areas (Table 2). Data collected for soils in North Rhine-Westphalia (NRW), Germany, in the context of an illegal application of PFC-containing waste to agricultural land showed that close to 90% of the soil samples were characterized by concentrations of PFOA + PFOS of a similar magnitude as the samples from Shanghai for which a direct contamination with e.g. sludge was not indicated (Fig. 4; LANUV, 2010). However, different to the results of Li et al. (2010), PFOS concentrations in NRW soils were commonly larger than PFOA concentrations with a PFOS/PFOA ratio of approximately 6.1 (LANUV, 2010). Concentrations larger than 500 ng g^{-1} were mostly associated with a heavy contamination of one site in Brilon-Scharfenberg. A recent study of biosolids and biosolid-amended soils by Sepulvado et al. (2011) suggests that in addition

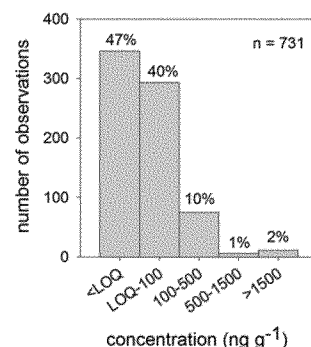


Fig. 4. Frequency distribution of PFOA + PFOS concentrations in soil samples collected following the illegal application of PFC-containing sludge to agricultural land in North Rhine-Westphalia, Germany (source: LANUV, 2010). LOQ, Limit of Quantification.

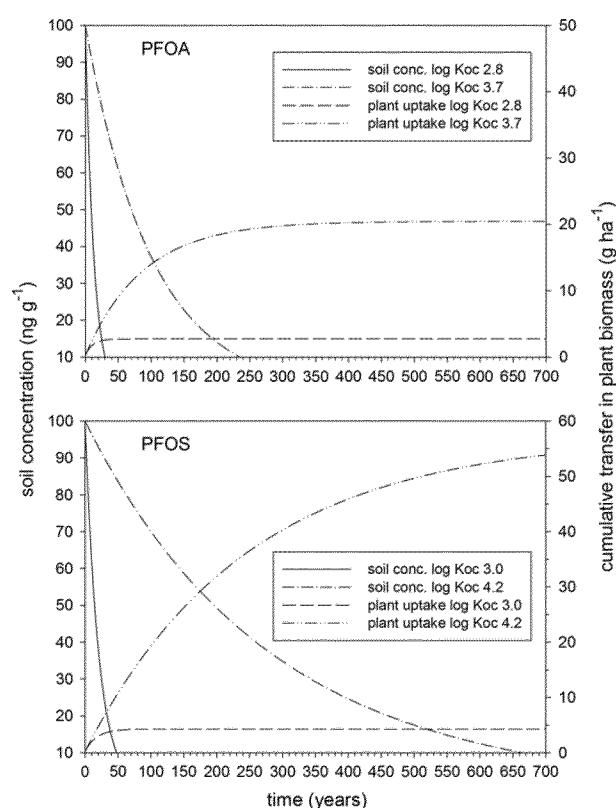


Fig. 5. Calculated dissipation of PFOA and PFOS from soil via leaching and plant uptake for different $\log K_{oc}$ distribution coefficients. Assumptions, Yearly plowed topsoil of 30 cm thickness, f_{oc} , 0.015, groundwater recharge, 250 mm year^{-1} , yield of *Lolium perenne*, $1.5 \text{ kg dry mass m}^{-2} \text{ year}^{-1}$, soil–plant transfer functions of Stahl et al. (2009) for the first cut.

to illegal application of waste, accidents, and spills, the application of biosolids to agricultural land represents an important source of PFOS in particular in soils (Table 2).

An important question is how sensitive the fate of soil contaminations with PFOA and PFOS is regarding the described variations in the $\log K_{oc}$ distribution coefficient. In order to assess the consequences of varying $\log K_{oc}$ coefficients, let us consider the topsoil (30 cm thick) of an arable site that is cropped with grass (*Lolium perenne*) for fodder production. We assume an organic carbon content of 1.5% weight ($f_{oc} = 0.015$) and a PFOA- or PFOS-content of 100 ng g^{-1} . Let the groundwater recharge equal 250 mm year^{-1} (BUNA, 2003), the yield of grass dry matter equal $1.5 \text{ kg m}^{-2} \text{ year}^{-1}$ (Ruhr-Stickstoff Aktiengesellschaft, 1988), and plant uptake

follows the soil–plant transfer function of Stahl et al. (2009) for the first cut of the grass. By calculating the plant uptake and leached amount of PFOA with a yearly time step using the average $\log K_{oc}$ of 2.8 from published laboratory studies, we can show that the time until the PFOA content in soil is reduced from 100 ng g^{-1} to 10 ng g^{-1} is approximately 30 years (Fig. 4). If we use instead our field-based, “global” $\log K_{oc}$ of 3.6 for PFOA, this period of time increases to approximately 230 years (Fig. 5). Because the PFOA is leached more slowly from the topsoil in the latter case, the amount of the original PFOA content in soil that is cumulatively removed with harvested plant biomass increases from 2.7 g ha^{-1} (for $\log K_{oc} = 2.8$) to 19.1 g ha^{-1} (for $\log K_{oc} = 3.7$; Fig. 5), which represents approximately 1% and 5% of the original mass contained in the soil, respectively. In the case of PFOS, considering our field-based “global” $\log K_{oc}$ of 4.2 instead of the average $\log K_{oc}$ of 3.0 derived from published laboratory experiments increases the time necessary to reduce the original concentration from 100 ng g^{-1} to 10 ng g^{-1} from approximately 50 years to 665 years (Fig. 5). The cumulative removal with harvested biomass increases from 4.3 g ha^{-1} (1%) to 53.4 g ha^{-1} (15% of original soil content), which compared to calculations using lab-based $\log K_{oc}$ values again differs by an order of magnitude.

2. Conclusions

Although data derived from laboratory sorption experiments with PFOA and PFOS can be successfully described with $\log K_{oc}$ distribution coefficients with surprisingly small variability, field-based observations of PFOA and PFOS concentrations in surface waters, sediments, wastewater treatment effluent and sewage sludge suggest that lab-based distribution coefficients potentially underestimate sorption of both compounds under field conditions. This underestimation can lead to a much too optimistic forecast of the rate of removal of PFOA and PFOS from soil with harvested biomass and drainage and in turn to a much longer residence time of these compounds in contaminated soils, e.g. following the phasing out of their production. This longer residence time would also result into an increased cumulative transfer of PFOA and PFOS from soils into crops. Nevertheless, the majority of soil contaminations with PFOA and PFOS will eventually drain to ground and surface water bodies.

Acknowledgements

This work was conducted in the framework of the “Safeguard” project, which is coordinated by GIGS and funded by the European Fund for Regional Development (EFRE) in the INTERREG IVA-program Germany – The Netherlands and by other national and regional agencies. These agencies are: Ministerium für Wirtschaft, Mittelstand und Energie des Landes NRW, Niedersächsisches Ministerium für Wirtschaft, Arbeit und Verkehr, Niederländisches Ministerium für Landwirtschaft, Natur und Lebensmittelsicherheit, Marktverband für Vieh, Fleisch und Eier (PVE), Lebensmittel- und Warenbehörde (VWA), Province Drenthe, Province Overijssel, Province Groningen, Province Fryslân, Province Gelderland, Province Nord-Brabant, Province Limburg. The research program is managed by the Euregio Rhein-Waal.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2013.02.024>.

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